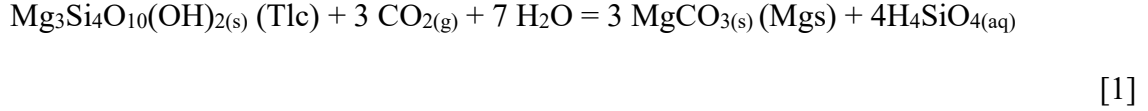


Supplementary File 1: Introduction to chemical equilibria and activity modelling

S1: INTRODUCTION TO CHEMICAL EQUILIBRIA AND ACTIVITY MODELLING

Activity modelling is used to determine equilibrium lines between pairs of minerals in a chemical system, *e.g.*, the reaction between talc (Tlc) and magnesite (Mgs):



The equilibrium constant of this reaction at a given pressure and temperature ($K_{P,T}$) is expressed as the activity of the products divided by the activities of the reactants:

$$K_{P,T} = \frac{a_{\text{MgCO}_3}^3 a_{\text{H}_4\text{SiO}_4(\text{aq})}^4}{a_{\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2} f_{\text{CO}_2}^3 a_{\text{H}_2\text{O}}^7}; \quad [2]$$

where a_X represents the activity of a given phase X , and the exponent represents the stoichiometric coefficient of the phase. Taking the logarithm of both sides yields:

$$\begin{aligned} \log K_{T,P} = & 3 \log a_{\text{MgCO}_3(\text{s})} + 4 \log a_{\text{H}_4\text{SiO}_4(\text{aq})} - \log a_{\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2(\text{s})} - 3 \log f_{\text{CO}_2(\text{g})} \\ & - 7 \log a_{\text{H}_2\text{O}(\text{l})}. \end{aligned} \quad [3]$$

Of particular interest is the effect of CO_2 fugacity and $\text{H}_4\text{SiO}_4(\text{aq})$ activity on the stability of talc *versus* magnesite. Therefore, [3] can be rewritten in the form of $y = mx + b$ with $\log f_{\text{CO}_2(\text{g})}$ as the independent variable x and $\log a_{\text{H}_4\text{SiO}_4(\text{aq})}$ as the dependent variable y :

$$\begin{aligned} \log a_{\text{H}_4\text{SiO}_4(\text{aq})} = & \frac{3}{4} \log f_{\text{CO}_2(\text{g})} \\ & + \frac{1}{4} [\log K_{P,T} - 3 \log a_{\text{MgCO}_3(\text{s})} + \log a_{\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2(\text{s})} + 7 \log a_{\text{H}_2\text{O}(\text{l})}]. \end{aligned} \quad [4]$$

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Assuming the activities for pure solids and liquids is unity, *i.e.*, $\log a_{H_2O(l)} = \log a_{MgCO_3(s)} = \log a_{Mg_3Si_4O_{10}(OH)_2(s)} = 0$ (assuming no solid solution) leads to a simplified expression:

$$\log a_{H_4SiO_4(aq)} = \frac{3}{4} \log f_{CO_2(g)} + \frac{1}{4} [\log K_{P,T}]. \quad [5]$$

Graphically, this represents a line with a slope of $\frac{3}{4}$ and intercept of $\frac{1}{4} [\log K_{P,T}]$. Plotting these lines for each set of phases produces an activity diagram.

To plot this line, the value of $\log K_{P,T}$ must be determined. At equilibrium, $\log K_{P,T}$ is directly proportional to the standard molar Gibbs free energy of the reaction ($\Delta_r G_{P,T}^0$):

$$\Delta_r G_{P,T}^0 = -\ln(10) RT \log K_{T,P}; \quad [6]$$

where R is the ideal gas constant ($8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). The $\Delta_r G_{P,T}$ can be determined by stoichiometric sum of the apparent molar Gibbs free energy of formation ($\Delta_a G_{P,T}$) values for the products minus those of the reactants.

The $\Delta_a G_{P,T}$ of each mineral and phase at the P, T of interest is given by the Legendre transform of the fundamental equation of thermodynamics (first and second laws of thermodynamics; *e.g.*, Berman 1988):

$$\Delta_a G_{P,T}^0 = \Delta_f H_{P,T}^0 - TS_{P,T}^0; \quad [7]$$

where $\Delta_f H_{P,T}^0$ = enthalpy of formation at the P and T of interest; and $S_{P,T}^0$ = entropy at the P and T of interest.

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The values for $\Delta_f H_{P,T}$ and $S_{P,T}$ are related to the standard state enthalpy of formation measured at reference conditions of 1 bar and 25°C ($\Delta_f H_{P_r,T_r}^0$ and S_{P_r,T_r}^0 , resp.), by considering the changes in H and S as a function of P and T (e.g., Berman 1988):

$$\Delta_a G_{P,T}^0 = \Delta_f H_{P_r,T_r}^0 - TS_{P_r,T_r}^0 + \int_{T_r}^T C_P dT - T \int_{T_r}^T \frac{C_P}{T} dT + \int_{P_r}^P V dP; \quad [8]$$

where: P_r, T_r = reference pressure (1 bar) and temperature (25°C); P, T = pressure and temperature of interest; C_P = heat capacity at constant pressure (i.e., isobaric); and V = volume. Note that the superscripted zero refers only to pure standard-state quantities and does not refer to the standard P - T conditions as usually denoted in physical chemistry. Given the above thermodynamic data, it is possible to calculate $\Delta_a G_{P,T}^0$ for each phase component in the reaction, yielding $\Delta_r G_{P,T}^0$ and $\log K_{P,T}$, which permits the plotting of the equilibrium line for talc *versus* magnesite in the above example.

From [8], the $\int_{T_r}^T C_P dT - T \int_{T_r}^T \frac{C_P}{T} dT$ terms require an equation of state for C_P vs. T . The value of C_P is variably expressed as polynomial functions of T of the form:

$$C_P = a + bT + cT^{-2} + dT^{-0.5} + eT^2 + fT^{-3} + gT^{-1}; \quad [9]$$

where a, b, c, d, e, f , and g are phase-specific empirical coefficients. Commonly used conventions include: (1) Maier-Kelley ($C_P = a + bT + cT^{-2}$, Maier & Kelley 1932), (2) Haas-Fisher ($C_P = a + bT + cT^{-2} + dT^{-0.5} + eT^2$, Haas & Fisher 1976, Robie & Hemingway 1995), (3) Berman-Brown ($C_P = a + dT^{-0.5} + cT^{-2} + fT^{-3}$, Berman & Brown 1985), and (4) Holland-Powell ($C_P = a + bT + cT^{-2} + dT^{-0.5}$; Holland & Powell 1985, Powell & Holland 1985). Where heat

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capacity data are not available, some thermodynamic data use the constant isobaric heat capacity assumption ($C_p = a$) or the Van't Hoff approximation ($C_p = 0$).

Similarly, the $\int_{P_r}^P V dP$ term in [8] requires an equation of state for the relationship between V vs. P and T . Many thermodynamic databases assume constant V for solids, given the minor deviations from surface conditions (*e.g.*, up to 5 kbar and 1000 °C). However, it is invalid to extrapolate constant V from surface conditions to the greater metamorphic P - T conditions (*e.g.*, to 100 kbar and 1000 °C), so equations of state for V have been implemented in metamorphic databases. For example, Berman (1988) uses the following relation:

$$\frac{V^{P,T}}{V^{P_r,T_r}} = 1 + \nu_1(P - P_r) + \nu_2(P - P_r)^2 + \nu_3(T - T_r) + \nu_4(T - T_r)^2, \quad [10]$$

where ν_1 , ν_2 , ν_3 , and ν_4 are empirical coefficients which describe the isothermal (ν_1 , ν_2) and isobaric (ν_3 , ν_4) compressibilities of the mineral of interest. Holland and Powell (1990, 1998, 2011) use more complex equations of state for V , but discussion of these is beyond the scope of this contribution.

For aqueous species, the refined Helgeson-Kirkham-Flowers (HKF) equations of state may be used instead of the heat capacity and volume equations of state listed above (Helgeson *et al.* 1981, Tanger & Helgeson 1988). The equations of state are built on the Born equation, which involves the Born solvation coefficient ω ; non-solvation volume coefficients a_1 , a_2 , a_3 , a_4 ; and non-solvation heat capacity coefficients c_1 , c_2 ; and charge Z (see Sverjensky 2019 for a comprehensive overview; Helgeson & Kirkham 1976).

As a note, caution must be taken when entering C_p and HKF coefficients from a thermodynamic database into a thermodynamic modelling software package because some of the

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C_p and HKF coefficients are reported in differing orders of magnitude (*e.g.*, for Maier-Kelley coefficients, b is commonly multiplied by 10^{-3} and c by 10^{-5}). Equally, it is important to check that the coefficient matches the correct corresponding polynomial in the equation for the C_p coefficients being selected.

Thus, for all chemical species, the following data are needed: $\Delta_f H_{P_r, T_r}^0$, S_{P_r, T_r}^0 , C_p , and V ($\Delta_a G_{P_r, T_r}^0$ can be calculated from the above data). Note that the S value used in aqueous geochemistry (Benson 1968, Helgeson *et al.* 1978) follows a different convention than that for metamorphic petrology (Powell & Holland 1985, Berman 1988). In metamorphic petrology, S is calculated using the third law of thermodynamics ($S_{P_r, T_r}^0 = \int_0^{T_r} \frac{C_p}{T} dT$) and does not include the entropies of the elements (S_{el}), whereas aqueous geochemistry includes the stoichiometric sum ($\sum_{el} n_{el}$) of S_{el} ($\Delta_f S_{P_r, T_r}^0 = \int_0^{T_r} \frac{C_p}{T} dT - \sum_{el} n_{el} S_{el}$), so it is necessary to verify that the database and software are using the same convention. For minerals and gases, both the coefficients expressing C_p as a function T , and the equation of state for V as a function of P and T are needed (if no relation for V is given, it is assumed to be constant). For aqueous species, the HKF coefficients (a_1 , a_2 , a_3 , a_4 , c_1 , c_2 , ω , and Z) may be used. Note that some software packages and thermodynamic databases do not use this thermodynamic data *per se*, instead employing the $\log K$ values related to the formation of minerals at various temperatures (*e.g.*, The Geochemist's Workbench™; Bethke 1995). Additionally, some $\log K$ databases account for the effects of P on $\log K$ to < 1 kbar (*e.g.*, *PHREEQC*; Appelo *et al.* 2014).

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